

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : H01M 8/10, C08J 5/22, B01D 69/12	A1	(11) International Publication Number: WO 00/63995 (43) International Publication Date: 26 October 2000 (26.10.00)
(21) International Application Number: PCT/US99/08627 (22) International Filing Date: 20 April 1999 (20.04.99) (71) Applicant: LYNNTECH, INC. [US/US]; 7610 Eastmark Drive, College Station, TX 77840 (US). (72) Inventor: CISAR, Alan, J.; 15603 Juniper Hollow Way, Cypress, TX 77429 (US). (74) Agents: STREETS, Jeffrey, L. et al.; Streets & Associates, P.O. Box 1612, Cypress, TX 77410-1612 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: PROCESS OF MAKING A COMPOSITE MEMBRANE (57) Abstract <p>The present invention relates to methods of fabricating composite membranes wherein at least one of the components is initially provided in the form of a precursor. The composite material comprising the precursor is processed to transform the precursor and obtain a membrane having a desired property. Including a thermoplastic precursor to a desired component, which itself is less thermoplastic, permits separate pieces of the membrane to be joined by welding or other thermal processes relying on the meltability of the components to achieve a bond. The invention also encompasses fabricating a reinforced ion conducting membrane by melting and mixing a non ion-conducting precursor to an ion-conducting polymer with an essentially inert polymer. The composite material is then processed to transform the non-ion conducting polymer into the ion-conducting form. The mixing of the precursor and the inert polymer may also be achieved by co-precipitating a solution of the precursor and a suspension of the inert polymer; impregnating the precursor onto the walls of the pores of a porous, essentially inert polymer; filling the pores of a porous, essentially inert polymer with a solution of comprising a non-ion conducting precursor to an ion conducting precursor and evacuating the solvent to substantially fill the pores of a porous, essentially inert polymer with the precursor; or melting the precursor, filling the pores of a porous essentially inert polymer with the melted precursor and cooling the precursor to form an essentially pore free composite membrane.</p> <div style="text-align: right; margin-top: 20px;"> $\begin{array}{c} \text{---} [\text{CF}_2\text{---CF}_2]_n \text{CF---CF}_2 \text{---} \\ \\ \text{O} \\ \\ \text{CF}_2 \\ \\ \text{CF---CF}_3 \\ \\ \text{O} \\ \\ \text{CF}_2 \\ \\ \text{CF}_2 \\ \\ \text{SO}_3\text{H} \end{array}$ </div>		

Best Available Copy

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

PROCESS OF MAKING A COMPOSITE MEMBRANE

Field of the Invention

The present invention relates generally to the field of ionically conducting separators. The invention particularly relates to methods and processes of fabricating composite membranes especially useful in electrochemical devices requiring a proton conductor such as fuel cells.

Background of the Invention

The operation of an electrochemical cell requires the occurrence of oxidation and reduction reactions which produce or consume electrons. In operation, an electrochemical cell is connected to an external load or to an external voltage source, and electric charge is transferred by electrons between the anode and the cathode through the external circuit. To complete the electric circuit through the cell, an additional mechanism must exist for internal charge transfer. This mechanism includes one or more electrolytes, which support charge transfer by ionic conduction. Electrolytes must be poor electronic conductors to prevent internal short circuiting of the cell.

One category of electrolytes particularly suitable for use in conjunction with electrochemical cells are proton exchange membranes (PEM). PEMs usually consist of a polymer matrix to which are attached functional groups capable of exchanging cations or anions. The polymer matrix generally consists of an organic polymer such as polystyrene, or other polytetrafluoroethylene (PTFE) analog. In general the material is acid with a sulfonic acid group incorporated into the matrix.

The apparent advantages of using PEMs in fuel cells are numerous. The solid electrolyte membrane is simpler and more compact than other types of electrolytes. Also, the use of a PEM instead of a liquid electrolyte offers several advantages, such as simplified fluid management and elimination of the potential of corrosive liquids. In systems using a PEM, the membrane also serves as an electronically insulating separator between the anode and cathode. However, a number of properties are desirable when using an acid ion exchange

membrane as an electrolyte. These include: high ionic conductivity with zero electronic conductivity; low gas permeability; resistance to swelling; minimal water transport; high resistance to dehydration, oxidation, reduction and hydrolysis; a high cation transport number; surface properties allowing easy catalyst bonding, and mechanical strength.

5 Conventional proton conducting membranes for use in polymer electrolyte membrane (PEM) fuel cells consist of homogeneous polymer films. Figures 1 and 2 are schematic diagrams depicting three examples of homogeneous polymer films used in polymer electrolyte membranes. The polymers depicted in Figure 1 were developed at DuPont and Dow. These polymers represent a class of compounds known as perfluorosulfonic acids (PFSA). These
10 polymers are fully fluorinated, *i.e.*, all of the sites occupied by hydrogen atoms in a conventional hydrocarbon polymer have been replaced by fluorine atoms. This makes the polymers extremely resistant to chemical attack.

PFSA polymers are generally synthesized by the copolymerization of a derivatized, or active, comonomer with tetrafluoroethylene, (TFE), as illustrated in Figure 3. After synthesis,
15 the thermoplastic polymer, which is both hydrophobic and electrochemically inert, is converted into the active ionomer by a base hydrolysis process, as illustrated. The result of this step is an ionomer in its salt form. This can be converted to the proton form by ion-exchange with a strong acid. The sulfonate functionalities ($R-SO_3^-$) act as the stationary counter charge for the mobile cations (H^+ , Li^+ , Na^+ , etc.) which are generally monovalent.

20 Another type of polymer, illustrated in Figure 2, is a derivatized trifluorostyrene (TFS), of the type developed by Ballard Advanced Materials. This polymer has a fully fluorinated backbone, but some of the side chains have hydrogen atoms.

The polymer is synthesized by copolymerizing derivatized and non-derivitized trifluorostyrene monomers, as illustrated in Figure 4. This process also produces an
25 electrochemically inactive thermoplastic. In this system the derivatized monomers create the inert sites while the non-derivitized monomers can be sulfonated, as illustrated in Figure 4. The result of this process is a proton conducting polymer.

Other homogeneous proton conducting polymers are tabulated in Table I. All of these polymers tend to have poor physical properties making them difficult to handle. For example,

sheets of the polymers are easily torn or punctured, thereby requiring a minimum usable thickness of about 2 mils (0.002", 0.05 mm).

Table I. Other Homogeneous Polymer Electrolytes

Manufacturer	Polymer
DAIS Corp.	Sulfonated styrene-butadiene block copolymer
Maxdem, Inc.	Sulfonated polyparaphenylene
(Not yet commercial)	Sulfonated side chains radiation grafted to PTFE

5 In U.S. Patent No. 5,547,551 Bahar *et. al* disclose a composite membrane fabricated by filling the void portion of a porous substantially inert polymer membrane with an ionically conducting polymer. This approach starts with a porous membrane fabricated from an inert polymer, such as polytetrafluoroethylene (PTFE) and converts it to an ion conducting
10 membrane by filling the pores with ionomer deposited from solution. This approach leads to thinner membranes, with membranes less than 1 mil (0.001", 0.025 mm) produced. These membranes are more conductive than pure PFSA membranes on a conductivity per unit area basis, but have lower specific conductivities. The advantage of these membranes is their strength. A 1 mil membrane produced using this technology is tougher than a conventional 5
15 mil homogeneous membrane.

In U.S. Patent No. 5,654,109, Plowman *et al.* disclose an alternate approach to the fabrication of reinforced membranes. In this approach, a core layer of a tough membrane material is clad with surface layers of highly ionically conductive polymer. Typically all of the layers are PFSA type materials, with the core layer having a significantly higher equivalent
20 weight than the surface layers. Although it would seem that the use of a high equivalent weight polymer would significantly impede the proton flux, it has been experimentally determined that a membrane with a core having an equivalent weight as much as 20% greater than the surface layers exhibits a conductivity equivalent to a solid membrane with the composition of the surface polymer.

While the above methods and processes may allow the fabrication of composite membranes that may present enhanced structural stability and ionic conductivity, the methods used do not allow the flexibility needed in fabricating composite membranes suitable for use in a wide range of applications. Thus there is a great need for membranes and membrane fabricating processes that allow greater flexibility in controlling the physical properties of the composite membranes.

Summary of the Invention

The present invention provides a method of making a composite membrane, comprising: (a) combining a first polymer component with a second polymer component; wherein the first polymer component is a non ion-conducting precursor to an ion-conducting polymer; and (b) converting the first polymer component from the non ion-conducting precursor to the ion-conducting polymer.

The combining of the polymeric components may comprise melting and mixing the polymers, co-polymerizing two or more monomers, co-precipitating a solution of a first polymer and a suspension of a second polymer, filling the pores of a porous polymeric matrix with a solution of a second polymer, or filling the pores of a porous polymeric matrix with a melted polymer.

The invention encompasses a process wherein the step of combining the first and second polymer components comprises mixing a solution of the first component and a suspension of the second component, co-precipitating the first and second polymer components to form a gelatinous mass, and drying the gelatinous mass. The dried gelatinous mass may further be sintered and/or pressed into a sheet, optionally at temperatures of about 150°C or about 300°C. Pressing the gelatinous mass into a sheet may be achieved by rolling the mass.

The processes of the invention may also combine the first and second polymer components by forming a solution of the first polymer component, filling the pores of the porous matrix with the solution; removing the solvent from the pores of the matrix to form an essentially pore-free composite material. Alternatively, the first and second polymer

components may be combined by melting the first polymer component, filling the pores of the porous matrix with the first polymer component, and cooling the polymer to form an essentially pore-free composite material.

The composite membranes formed by the processes of the invention may comprise
5 regions essentially made of the first polymer component and regions essentially made of the second polymer component. Further, the first polymer component may form an ion-conducting path, generally a hydrophilic path capable of transporting ions through the membrane.

The invention also encompasses a method of making a composite membrane,
10 comprising: (a) initiating a living chain co-polymerization of a first monomer and a second monomer, wherein the first monomer is a non-derivatizable monomer and the second monomer is a non ion-conducting precursor to an ion-conducting monomer; (b) propagating the polymerization to form a co-polymer chain comprising a given number of non-derivatizable monomers and a given number of precursor monomers; (c) fabricating a
15 membrane from the co-polymer chain; and (d) transforming at least a portion of the non ion-conducting precursor monomers into ion-conducting monomers. The non-derivatizable monomers and precursor monomers may be randomly distributed along the co-polymer chain. Depending on the application of the composite membrane, the number of non-derivatizable monomers in the co-polymer chain may be greater or lower than the number of precursor
20 monomers in the co-polymer chain. The process of the invention allow the fabrication of composite membranes wherein the co-polymer chain comprises regions wherein most or all of the monomers are non-derivatizable monomers and regions wherein most or all of the monomers are precursor monomers or ion-conducting monomers obtained by transforming precursor monomers. The regions comprising precursor monomers or ion-conducting
25 monomers obtained by transforming precursor monomers may form an ion-conducting path, generally a hydrophilic path capable of transporting ions through the composite membrane.

Finally, the processes of the invention are applicable to any combination of polymeric components as well as combination of a polymeric component and a non polymeric component. For example, the first component may a precursor to an ion conducting polymer

component selected from long side chain perfluorosulfonic acid, short side chain perfluorosulfonic acid, trifluorostyrene, partially derivatized trifluorostyrene, polystyrene, and mixtures thereof. The second polymer component may be a substantially inert polymer selected from polytetrafluoroethylene (PTFE), perfluoroalkoxy derivative of PTFE (PFA), fluorinated ethylene-propylene copolymer (FEP), polyvinyl chloride, polyvinyl dichloride, polyvinyl fluoride (PVF), polystyrene, polytrifluorostyrene (TFS), polyether ketone, polyether sulfone, polyparaphenylene, and mixtures thereof. When the second component is a porous matrix, the second component may be an inorganic material selected from fiber glass, fibrous quartz, rock wool, fibrous alumina, other fibrous silicates or alumino-silicates, and mixtures thereof.

Brief Description of the Drawings

So that the above recited features and advantages of the present invention can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to the embodiments thereof which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

Figure 1 is the generic chemical structure for perfluorinated sulfonic acid (PFSA) polymers used as PEM membranes.

Figure 2 represents the chemical structure of derivatized trifluorostyrene (TFS) having a fully fluorinated backbone, but some of the side chains have hydrogen atoms.

Figure 3 is a chemical equation for synthesizing PFSA polymers by the copolymerization of a derivatized, or active, comonomer with tetrafluoroethylene.

Figure 4 is a chemical equation for synthesizing the TFS of Figure 2 by copolymerizing derivatized and non-derivatized trifluorostyrene monomers.

Detailed Description of the Preferred Embodiment

The present invention provides a process of fabricating composite membranes. The process of the invention allow greater flexibility in adjusting physical properties of the membrane, such as the mechanical strength and ionic conductivity. The membranes fabricated by the methods of the invention are composite membranes comprising at least two components. Controlling the proportion of each component in the composite membrane allows for adjusting the physical properties conferred to the composite membrane by the particular component. For example, one component in the composite membrane may be essentially associated with the mechanical strength of the membrane, while another component may be essentially associated with the ionic conductivity properties of the membrane. Yet other components may provide control or influence of other qualities of the membrane. While the present specification focuses on components associated with the physical strength and ionic conductivity of the composite membrane, the methods of the invention may be readily used in fabricating composite membranes having components associated with other physical or chemical qualities of the membrane. Such methods of fabricating composite membranes are within the scope of the present invention.

One aspect of the invention provides processes of fabricating composite membranes wherein at least one of the components is initially added to the composition in the form of a precursor. The composition comprising the precursor may then be processed to transform the precursor and obtain a membrane having a desired property. Obtaining an intermediate composition comprising precursors to one or more components may provide more flexibility in fabricating composite membranes with properties tailored for use in a particular application.

The properties of the precursor may allow the use of certain processing methods that may be otherwise impractical or difficult to implement. For example, fabricating a composite membrane by including a thermoplastic precursor to a desired component, which itself may be less thermoplastic, may permit separate pieces of the membrane to be joined by welding or other thermal processes relying on the meltability of the components to achieve a bond.

Properties that may be better controlled by fabricating membranes through the processes of the invention include, but are not limited to, physical strength, ionic conductivity, shape stability, resistance to oxidation, durability, etc. The components in the composite membranes that may be fabricated by the methods of the invention may be organic polymers or non-polymeric substrates, such as quartz wool and woven alumina fibers.

The methods of the invention allow for combining the components in the composite membrane over a wide range of ratios between the components. Depending on the use of the membrane, a certain physical property may be more desirable than the other and the proportions of the components in the membrane may be adjusted to obtain the desired balance between the physical properties provided by each component.

For example, in a composite polymer membrane having an inert component and an ion conducting component, when high ion conductivity is the more desirable quality, the proportion of the ion conducting polymer may be maximized and the portion of the inert polymer minimized. Conversely, in applications where the structural properties may be more important, the proportion of the inert component may be maximized and the proportion of the conducting component minimized.

Since the methods of the invention allow intimate mixing of the components in the composite membrane, a component may be able to confer to the composite membrane its qualities even when the component is provided in minimal proportions. The methods of the invention may allow the fabrication of polymer compositions where the proportion of an individual component may vary between about 1 wt. % and about 99 wt %.

For example, in applications, such as fabricating sensing devices, where ruggedness may be a more useful property than high conductivity, the amount of active polymer, used in the composite membrane, may be decreased to the minimal proportion capable of producing a continuous network. Conversely, in applications, such as the fabrication of power generation devices, where conductivity may be the more desirable property, the amount of inert polymer may be decreased to the smallest proportion capable of conferring to the composite membrane the desired structural integrity.

In PEM fuel cells the membrane electrolyte may be exposed to extremely oxidizing conditions. Not only may one side of the membrane be exposed to air at elevated temperatures, but the fuel cell reactions themselves may produce trace levels of hydrogen peroxide and peroxy radicals. These compounds are extremely powerful oxidizers that may readily attack hydrocarbons and partially halogenated polymers. Thus it may be highly advantageous to use composite membranes with controlled resistance to oxidation.

Controlling the membrane's resistance to oxidation may be achieved by including in the composite membrane a polymer having high resistance to oxidation and adjusting the proportion of such a polymer to achieve the desired qualities while conserving other qualities such as ionic conductivity, thickness and structural integrity. Perfluorinated materials, such as PTFE and PFSA, are highly resistant to oxidation. Adjusting the proportion of these polymers in a composite membrane may allow better control of the chemical and structural properties of the membrane.

While some polymers, such as PFSA polymers, may have high ionic conductivity, they also have a strong affinity for water and consequently undergo a significant change in size when the amount or activity of the water in the environment changes. Controlling the shape of composite membranes comprising a polymer, such as a PFSA polymer, may be achieved by including in the membrane a component whose shape does not change with the activity of the water contacting the membrane. Further, the processes of the invention may allow the fabrication of composite membranes where the change in the size of one component may be limited by the presence of another component in the membrane.

The processes of the invention allow better use of lower equivalent weight ionomers. Lowering the equivalent weight of an ionomer generally leads to an improvement in conductivity. But the gain in ionic conductivity provided by low weight ionomers is often offset by the loss of certain physical qualities, such as tear strength and puncture resistance. Composite membranes fabricated by the processes of the invention may comprise a reinforcing component that supplies structural integrity to the membrane while the low molecular weight ionomer may confer to the membrane the desired ionic conductivity.

Another aspect of the invention provides a process of fabricating a reinforced ionically conducting membrane by blending at least two thermoplastic polymers, forming a membrane, and derivatizing one of the components of the blend. For example, a composite membrane having controlled ion conductivity and structural integrity may be fabricated by melting a precursor to an ion conducting polymer, such as the sulfonyl fluoride intermediate form of a PFSA polymer or the unsulfonated form of a trifluorostyrene (TFS) polymer, with an inert polymer providing structural strength, such as PTFE. The two polymers may be thoroughly blended, and fabricated into a membrane by fabrication methods such as extrusion or casting. The ionically conducting membrane may then be obtained by hydrolyzing the precursor with a strong base in the case of sulfonyl fluoride precursors to PFSA membranes, or by sulfonating the precursor to TFS in TFS containing membranes.

While it may be advantageous to blend polymers that are fully miscible, The processes of the invention may also be applied to the blending of polymers that are partially miscible or non miscible. Fully miscible polymers may be more easily combined in any proportions, while partially miscible polymers may be easily combined over only the range of their full miscibility. Outside the fully miscible range, or if the polymers are immiscible, the polymers may still be combined by mixing at high shear. In the case of viscous materials like high molecular weight polymers, high shear is defined as the shear at which the immiscible polymers may be spread as a finely dispersed mixture.

The composite membranes fabricated by the methods of the invention may comprise randomly blended polymers as well as alternating blocks, each block comprising essentially one particular polymer. For example, a composite membrane may be fabricated by forming, within each molecule, regions of pure PTFE and regions of low equivalent weight copolymer. The pure PTFE regions may crystallize to form a reinforcing matrix, while the low equivalent weight regions may furnish high proton conductivity paths. The methods of the invention comprise extruding and processing a polymer-block type composite membrane using the same techniques that may be used in fabricating a conventional random polymer membrane.

A further aspect of the invention provides a process of co-polymerizing two or more monomers to form a co-polymer chain molecule which may be fabricated into a composite

membrane. Each monomer may provide the composite membrane with a particular set of qualities. Co-polymerizing two or more monomers may allow the fabrication of a membrane having the combined qualities of the monomers. One or more of the monomers may first be present in the form of a precursor having thermoplastic properties that would allow easier fabrication of the composite membrane. After the membrane is formed, the precursor monomers may be transformed into a form allowing the composite membrane to have one or more desired qualities associated with the transformed precursor.

The processes of the invention may use any copolymerization technique to form copolymer chain molecule that may be used in fabricating a composite membrane. One method of copolymerization that may be used in the processes of the invention comprises: (a) initiating a radical polymerization process using a monomer not amenable to derivatization or functionalization as the only monomer; (b) allowing the polymerization to proceed to form chains or blocks of a desired length; (c) adding a substantial amount of one or more additional monomers and continuing the polymerization to produce segments or blocks on the same polymer chains which are rich in locations capable of being derivatized or functionalized to produce a polymer having a low equivalent weight when converted into an ion exchangeable form. Optionally the co-polymerization method may further comprise (d) returning the feed composition to the original monomer not amenable to derivatization or functionalization and extending the chains with additional blocks not capable of functionalization, and/or (e) adding a substantial amount of one or more additional monomers and continuing the polymerization to produce segments or blocks on the same polymer chains which are rich in locations capable of being derivatized or functionalized to produce a polymer having a low equivalent weight when converted into an ion exchangeable form. The copolymer chains may then be used in fabricating a composite membrane that may be processed to transform the precursor monomers into a form that may confer to the composite membrane certain desirable qualities.

For example, a composite membrane may be fabricated by forming, within each molecule, regions of pure PTFE and regions of low equivalent weight copolymer. The pure PTFE regions may crystallize to form a reinforcing matrix, while the low equivalent weight regions may furnish high proton conductivity paths. The methods of the invention comprise

extruding and processing a polymer-block type composite membrane using the same techniques that may be used in fabricating a conventional random polymer membrane.

Another aspect of the invention provides a process of fabricating a composite membrane comprising mixing a solution of a first polymer with a suspension of a second polymer. The mixture may then be treated to convert the first and/or second polymers into an insoluble pseudo-thermoplastic derivative that precipitates to form a gelatinous to solid mass. The gelatinous to solid mass may be filtered from the supernatant liquid, washed and dried. The dried mass may be fabricated into a sheet and sintered. The sintered sheet may be fabricated into a composite membrane. The pseudo-thermoplastic derivatives that have been formed in the early phases of the process may be converted back into their original form so that a composite membrane having the properties of the original components of the mixture may be formed.

For example, a composite membrane comprising an ion conducting component and an inert component may be formed by mixing a polymer, such as Nafion, which is ion conducting, with a suspension of a polymer, such as PTFE, which may provide the structural reinforcing element in the membrane. The mixture may be processed to the perfluorosulfonate ionomer from the proton form, or other form with simple ions, to the tetraalkylammonium form which is a pseudo-thermoplastic, and not ionically conductive. The mixture may then be precipitated to form a gelatinous to solid mass. The gelatinous to solid mass may be fabricated into a sheet and sintered. The sintered sheet may be fabricated into a composite membrane and the perfluorosulfonate component converted back to an ion conducting form through the use of a strong acid.

Yet another aspect of the invention provides a process of fabricating a composite membrane comprising an ion conducting component and a structurally stable matrix. The matrix must be porous and is preferably substantially inert. The pores or voids in the matrix may be filled with a polymer, such as a non ion-conducting thermoplastic precursor to a polymer that is ion conducting. After filling the pores of the matrix with the precursor, the precursor may be processed and transformed into the ion conducting polymer. The process allows for the fabrication of a reinforced ionically conducting membrane with controlled ion

exchange properties, which may be more difficult to obtain by directly filling the pores of the matrix with the non-thermoplastic ion conducting form of the polymer.

The present invention provides impregnation steps that may be carried out in several ways. For example, when the "filling" polymer is soluble in either a pure solvent or a blend of solvents, a solution of the polymer may be produced. The pore of the substrate may be filled with the solution. The solvent may then be evaporated to leave the polymer filling the pores of the matrix.

In composite membranes having components with significantly different melting temperatures, the "filling" polymer may be melted and deposited in the pores of the matrix. The polymer may then be cooled off to form a solid filler occupying the void in the matrix. Since there is no solvent to be removed, the process may allow fabricating a pore free membrane in less steps than would be otherwise required by the solution impregnating version of the present invention.

Impregnating a porous matrix with a precursor to an ionically conducting polymer may present several advantages. Fabricating an intermediate composite membrane comprising the thermoplastic components may permit separate pieces made of the intermediate composite material to be joined by welding or other thermal processes relying on the meltability of the components to achieve a bond. The matrices may be either polymeric or inorganic in nature. It is important that any substrate used not only be substantially inert to degradation during the hydrolysis step, but if the resulting membrane is to be used in the proton form, the substrate must be inert to degradation by acids as well.

The processes of the invention may be implemented in the fabrication of composite membranes comprising a variety of polymers. Polysulfone is a thermoplastic with excellent heat resistance and a high heat deflection temperature (150°C). Composite membranes made with a polysulfone matrix may be less subject to creep than those made with PTFE matrices. Other polymers, such as polymethylmethacrylate, silicone rubber, and polyvinyl chloride, may also be combined with other components to form composite membranes fabricated by the processes of the invention. This listing is not exhaustive. There are other polymers which could be used in the same manner as those described here. The use of other polymers as the

binder phase to produce membranes like those claimed here is considered to be obvious to one skilled in the art and within the scope of the present invention.

For example, a polymer, such as the sulfonyl fluoride intermediate form of a PFSA polymer, or the unsulfonated form of a TFS polymer, may be impregnated into the void portion of a porous, but substantially inert substrate sheet or other fabricated shape. After impregnation, the added polymer may be converted into its active ion exchange form. The final product may be suitable for use in a variety of electrochemical cells and other devices where the ability to function as an ion exchanger and good physical strength may be desirable properties.

The choice of a particular polymer or matrix may be dictated by the type of application where the composite membrane is intended to be used. When the membrane is used in a fuel cell, it is important that the polymer remain flexible under fuel cell operating conditions, and that any size change that occurs with changing conditions be relatively small.

The following example shows the function of this invention and some of its preferred embodiments.

Example 1 (hypothetical)

Powdered or pelletized PTFE may be combined with a powdered or pelletized sulfonyl fluoride polymer, such as the perfluorinated short side chain polymer (PFSF) developed by the Dow Chemical Company, having an equivalent weight of about 700 Daltons per sulfonyl fluoride group. These polymers may be melted and combined in a ratio of 40 wt. % PTFE to 60 wt. % PFSF. Since these polymers may be completely miscible, they easily form a homogeneous solution on melting and blending (at about 360°C). The composite polymer may then be extruded to form a sheet of about 75% of the thickness desired for the final ionomer containing polymer in its dry form.

The thermoplastic film may be converted to the ionomer form by hydrolyzing in a solution of 25 wt. % NaOH at 85°C. While a solid PFSF membrane may be converted to its ionomer form in less than six hours, the composite membrane requires at least 24 hours to

fully hydrolyze. Carrying out the ion exchange reaction to convert the salt form of the ionomer to the acid form is slower as well. Two exchange cycles, of six hours each, using fresh acid (25 wt. % H_2SO_4) may be necessary to convert the sodium polymer to the proton form. After washing in deionized water (100°C for one hour) three times, the PTFE-PFSA composite membrane is ready for use.

Example 2 (hypothetical)

A composite membrane may be fabricated by combining a quantity of T-60 PTFE suspension (typically 60% solid) with a solution of 5 wt. % Nafion ionomer having an equivalent weight of 950 Daltons (in proton form) and adding extra water. The proportion of each component in the mixture may be adjusted to achieve the desired ratio for the final component. The acid functions in the PFSA polymer may be neutralized with a stoichiometric amount of tetrabutylammonium hydroxide. This will precipitate the Nafion as a gelatinous mass, and bring the suspended PTFE out of suspension as well. The gelatinous mass may be transferred to a filtration apparatus to remove the excess water, and wash the material.

The sequence of the mixing and precipitating steps is optional. If desired, the PFSA may be neutralized and precipitated as a gel before the PTFE is added. If this sequence is used, dry powdered PTFE may be substituted for the suspension.

The layer obtained by the above process may then be fabricated into a membrane. This may be accomplished by calendaring, or pressing. In either case, the material may be compressed either hot or cold, but it must be heated to over 320°C to drive off any surfactant that may have been used to keep the PTFE in suspension and to sinter the PTFE. If the press or rollers are not heated, the heating may be carried out separately in a separate step in an oven. The material should be protected from oxidation at any time that it is above a temperature above 150°C.

The membrane produced by this process is a blend of PTFE and perfluorosulfonate, the perfluorosulfonate in the tetrabutylammonium form, which is a water repellent thermoplastic, not a hydrophilic material. It may be converted back to the active, proton conducting form by boiling the membrane in nitric acid for 24 to 48 hours. The acidified

material may then be washed thoroughly and used in the fabrication of membrane electrode assemblies.

Example 3 (hypothetical)

A perfluorosulfonic acid (PFSA) polymer in its sulfonyl fluoride form (PFSF), as
5 illustrated herein, is a thermoplastic. This material may be dissolved in an appropriate fluorinated solvent, such as perfluorobutylmethyl ether ($C_4F_9OCH_3$) or perfluorodecalin ($C_{10}F_{18}$). The solution may be impregnated into the pore structure of a porous expanded PTFE sheet, such as GoreTex[®], (W. L. Gore and Associates, Newark, DE.) and the solvent evaporated to leave the PFSF polymer filling the pores.

10 Since the PFSF polymer has only limited solubility, a single treatment may not be adequate to produce a pore free membrane. In this case, the treatment process can be repeated, with multiple cycles used, if necessary, to produce a pore-free sheet.

The PFSF material may then be converted into its sulfonate form by base hydrolysis. By controlling the time and temperature of the hydrolysis the degree of conversion can be
15 controlled, furnishing a post-polymerization method of controlling the equivalent weight of the final PFSA membrane and a way to make membranes with a tailorable, equivalent weight profile. Within certain limits, it is also possible to adjust the equivalent weight later. (*i.e.* If the PFSF material is not fully hydrolyzed initially, it can be at a later date.) This ionomer can be converted to the acid, or proton form, by ion exchange using an excess of a strong acid as
20 a proton source.

The composite membranes produced by this method will have the PFSA material more tightly bound into the final structure than those produced by impregnating a solution of ionomer into the pores, since the thermoplastic PFSF polymer will initially bond tightly to the PTFE matrix and because the expansion that occurs during the hydrolysis process will aid in
25 keying the resulting PFSA material into the pores of the matrix. The resulting membranes are suitable for use in electrochemical devices such as fuel cells.

While the foregoing is directed to the preferred embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims which follow.

What is claimed is:

- 1 1. A method of making a composite membrane, comprising:
 - 2 (a) combining a first polymer component with a second polymer component; wherein
 - 3 the first polymer component is a non ion-conducting precursor to an ion-conducting polymer;
 - 4 and
 - 5 (b) converting the first polymer component from the non ion-conducting precursor to
 - 6 the ion-conducting polymer.
- 1 2. The process of claim 1 wherein the combining of the components comprises melting
- 2 and mixing the polymers.
- 1 3. The process of claim 2 wherein the second polymer component comprises a
- 2 substantially inert polymer.
- 1 4. The process of claim 3 wherein the substantially inert polymer is selected from
- 2 polytetrafluoroethylene (PTFE), perfluoroalkoxy derivative of PTFE (PFA), fluorinated
- 3 ethylene-propylene copolymer (FEP), polyvinyl chloride, polyvinyl dichloride, polyvinyl
- 4 fluoride (PVF), polystyrene, polytrifluorostyrene (TFS), polyether ketone, polyether sulfone,
- 5 polyparaphenylene, and mixtures thereof.
- 1 5. The process of claim 1 wherein the ion conducting polymer component is selected
- 2 from long side chain perfluorosulfonic acid, short side chain perfluorosulfonic acid,
- 3 trifluorostyrene, partially derivatized trifluorostyrene, polystyrene, and mixtures or
- 4 copolymers thereof.

1 6. The process of claim 1 wherein the first component comprises a polymer capable of
2 being dissolved in a solvent and the second component comprises a polymer capable of
3 forming a suspension.

1 7. The process of claim 6 wherein the step of combining the first and second polymer
2 components comprises mixing a solution of the first component and a suspension of the
3 second component, co-precipitating the first and second polymer components to form a
4 gelatinous mass, and drying the gelatinous mass.

1 8. The process of claim 7 wherein the first polymer component is selected from long side
2 chain perfluorosulfonylfluoride, short side chain perfluorosulfonylfluoride, trifluorostyrene,
3 partially derivatized trifluorostyrene, polystyrene, poly-bis[{perfluoroalkyl)sulfonyl]imide and
4 its derivatives, perfluoro-ethylene-1,2-bis-phosphonic acid derivatives, and mixtures thereof.

1 9. The process of claim 7 wherein the second polymer component is selected from
2 polytetrafluoroethylene (PTFE), perfluoroalkoxy derivative of PTFE (PFA), fluorinated
3 ethylene-propylene copolymer (FEP), polyvinyl chloride, polyvinyl dichloride, polyvinyl
4 fluoride (PVF), polystyrene, polytrifluorostyrene (TFS), polyether ketone, polyether sulfone,
5 polyparaphenylene, and mixtures thereof.

1 10. The process of claim 7 further comprising rolling the dried gelatinous mass into a
2 sheet.

1 11. The process of claim 10 wherein the rolling is carried out at a temperature of about
2 150°C.

1 12. The process of claim 11 further comprising sintering the dried gelatinous mass at a
2 temperature higher than 150°C.

1 13. The process of claim 10 wherein the rolling is carried out at a temperature of about
2 300°C.

1 14. The process of claim 13 further comprising sintering the dried gelatinous mass at a
2 temperature higher than 300°C.

1 15. The process of claim 7 further comprising pressing the dried gelatinous mass into a
2 sheet.

1 16. The process of claim 1 wherein the first polymer component comprises a soluble
2 polymer and the second polymer component comprises a porous matrix.

1 17. The process of claim 16 wherein the step of combining the first and second polymer
2 components comprises forming a solution of the first polymer component, filling the pores of
3 the porous matrix with the solution; removing the solvent from the pores of

1 the matrix to form an essentially pore-free composite material.

1 18. The process of claim 16 wherein the porous matrix comprises an organic polymer.

1 19. The process of claim 16 wherein the matrix polymer is selected from
2 polytetrafluoroethylene (PTFE), perfluoroalkoxy derivative of PTFE (PFA), fluorinated
3 ethylene-propylene copolymer (FEP), polyvinyl chloride, polyvinyl dichloride, polyvinyl
4 fluoride (PVF), polystyrene, polytrifluorostyrene (TFS), polyether ketone, polyether sulfone,
5 polyparaphenylene, and mixtures thereof.

1 20. The process of claim 16 wherein the porous matrix comprises an inorganic material.

1 21. The process of claim 20 wherein the inorganic material is selected from fiber glass,
2 fibrous quartz, rock wool, fibrous alumina, other fibrous silicates or alumino-silicates, and
3 mixtures thereof.

1 22. The process of claim 16 wherein the soluble polymer is selected from long side chain
2 perfluorosulfonylfluoride, short side chain perfluorosulfonylfluoride, trifluorostyrene, partially
3 derivatized trifluorostyrene, and polystyrene.

1 23. The process of claim 1 wherein the second polymer component comprises a porous
2 polymer matrix, and wherein the step of combining the first and second polymer components
3 comprises melting the first polymer component, filling the pores of the porous matrix with the
4 first polymer component, and cooling the polymer to form an essentially pore-free composite
5 material.

1 24. The process of claim 23 wherein the second polymer component comprises an
2 inorganic material.

1 25. The process of claim 24 wherein the inorganic material is selected from fiber glass,
2 fibrous quartz, rock wool, fibrous alumina, other fibrous silicates or alumino-silicates, and
3 mixtures thereof.

1 26. The process of claim 1 wherein the composite membrane comprises regions essentially
2 made of the first polymer component and regions essentially made of the second polymer
3 component.

1 27. The process of claim 26 wherein the regions essentially made of the first polymer
2 component form an ion-conducting path capable of transporting ions through the membrane.

1 28. The process of claim 27 wherein the ion-conducting path comprises a hydrophilic path.

1 29. A method of making a composite membrane, comprising:

2 (a) initiating a living chain co-polymerization of a first monomer and a second
3 monomer, wherein the first monomer is a non-derivatizable monomer and the second
4 monomer is a non ion-conducting precursor to an ion-conducting monomer;

5 (b) propagating the polymerization to form a co-polymer chain having at least one
6 region essentially comprised of non-derivatizable monomers and at least one region
7 essentially comprised of precursor monomers;

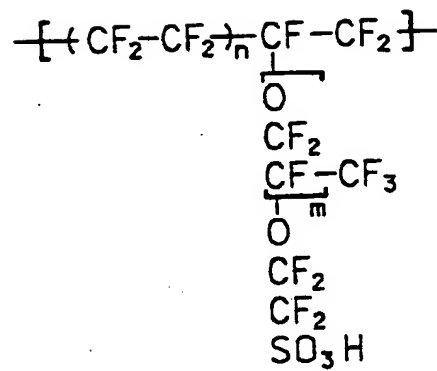
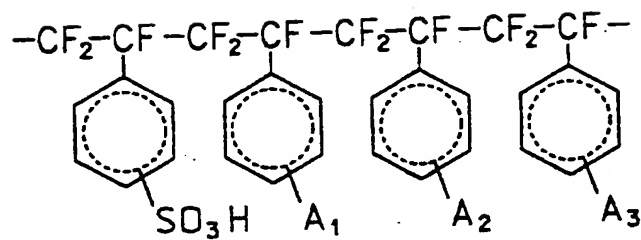
- 8 (c) fabricating a membrane from the co-polymer chain; and
9 (d) transforming at least a portion of the non ion-conducting precursor monomers into
10 ion-conducting monomers.

1 30. The process of claim 29 wherein the number of non-derivatizable monomers in the co-
2 polymer chain is greater than the number of precursor monomers in the co-polymer chain.

1 31. The process of claim 29 wherein the number of non-derivatizable monomers in the co-
2 polymer chain is lower than the number of precursor monomers in the co-polymer chain.

1 32. The process of claim 29 wherein the regions comprising precursor monomers or ion-
2 conducting monomers obtained by transforming precursor monomers form an ion-conducting
3 path capable of transporting ions through the composite membrane.

1 33. The process of claim 32 wherein the ion-conducting path comprises a hydrophilic path.

**FIG. 1****FIG. 2**

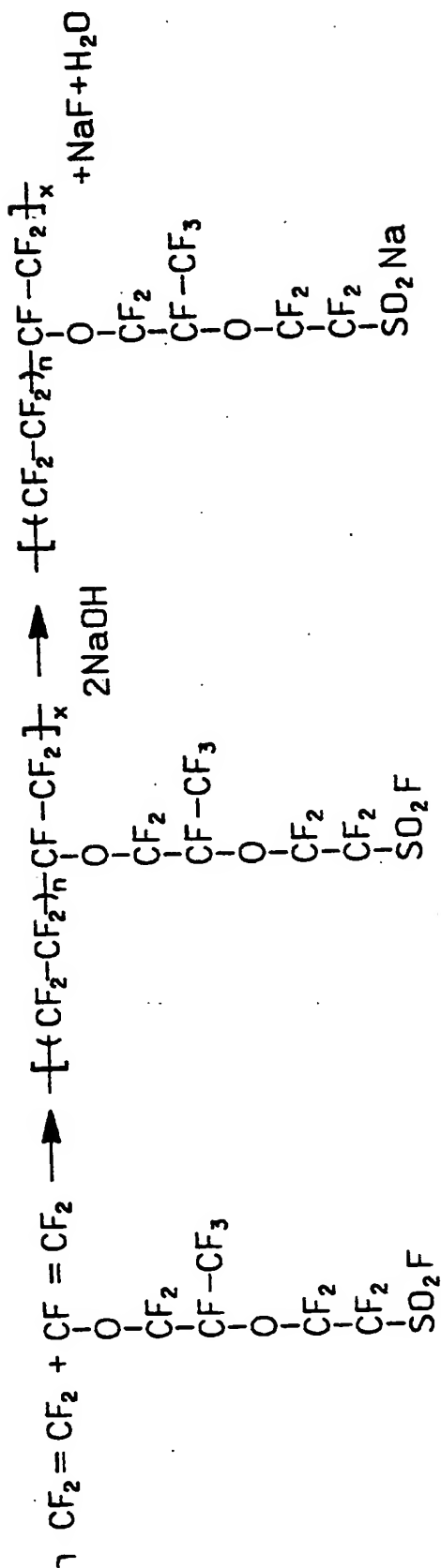


FIG. 3

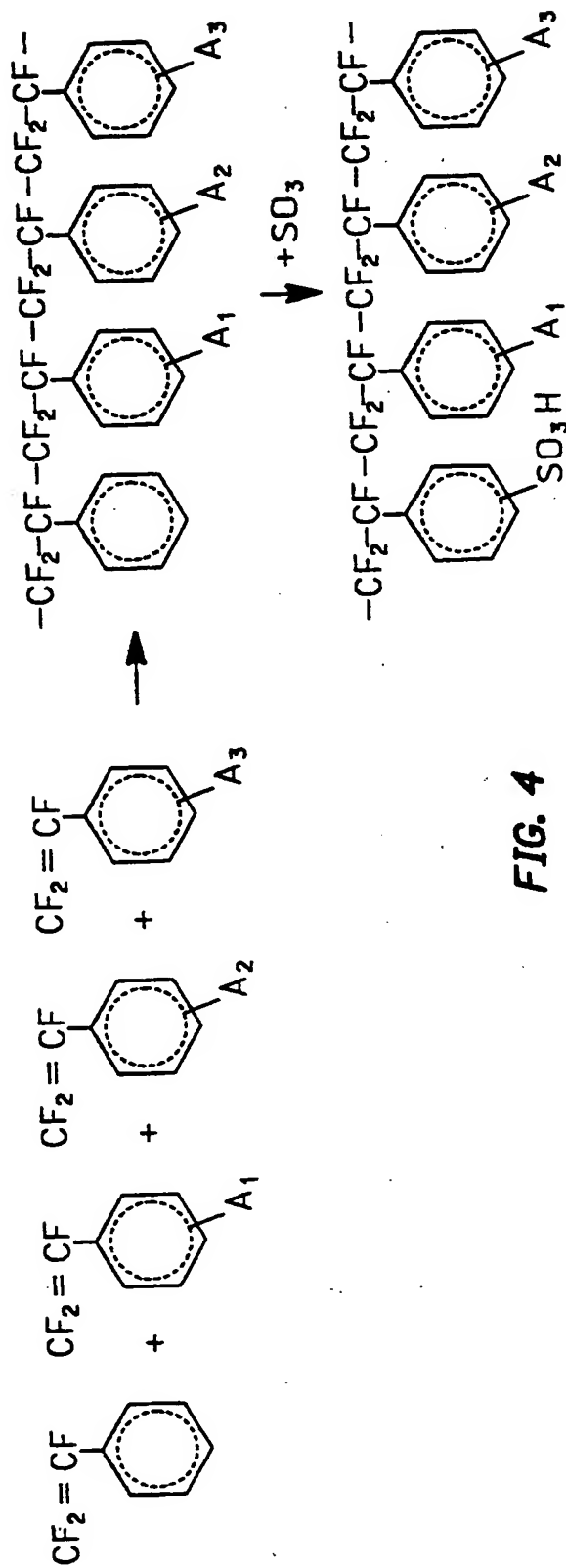


FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/08627

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M8/10 C08J5/22 B01D69/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M C08J B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 25369 A (BALLARD POWER SYSTEMS ;STONE CHARLES (CA); STECK ALFRED E (CA)) 17 July 1997 (1997-07-17)	1-23, 26-28
Y	page 4, line 6-21 page 8, line 1 -page 9, line 9 page 16, line 1-14 page 23, line 7 -page 25, line 26 ---	24
X	US 5 746 954 A (AIKMAN JR ROBERT E) 5 May 1998 (1998-05-05) column 3, line 13-44 column 4, line 65 -column 5, line 11 ---	1-23, 26-28
X	US 5 654 109 A (PLOWMAN KEITH R ET AL) 5 August 1997 (1997-08-05) cited in the application column 8, line 6-21 column 9, line 62 -column 10, line 8 --- -/-	1-23, 26-28

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

15 December 1999

Date of mailing of the international search report

19/01/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Engl, H

INTERNATIONAL SEARCH REPORT

Inter nal Application No

PCT/US 99/08627

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	US 5 447 636 A (BANERJEE SHOIBAL) 5 September 1995 (1995-09-05)	1-23, 26-28
Y	column 7, line 8-57 example 1 ---	24
Y	WO 97 41168 A (GORE & ASS) 6 November 1997 (1997-11-06) page 11, line 31-37 ---	24
A	US 4 720 334 A (DUBOIS DONALD W ET AL) 19 January 1988 (1988-01-19) the whole document -----	1-28

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/08627

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9725369 A	17-07-1997	US 5834523 A AU 704923 B AU 1187297 A CA 2240495 A EP 0882088 A US 5985942 A	10-11-1998 06-05-1999 01-08-1997 17-07-1997 09-12-1998 16-11-1999
US 5746954 A	05-05-1998	BR 9610418 A CA 2231142 A CN 1199409 A EP 0874873 A NO 981006 A WO 9709373 A	06-07-1999 13-03-1997 18-11-1998 04-11-1998 06-05-1998 13-03-1997
US 5654109 A	05-08-1997	NONE	
US 5447636 A	05-09-1995	CA 2176560 A DE 69408870 D DE 69408870 T EP 0734410 A JP 9506662 T WO 9516730 A	22-06-1995 09-04-1998 17-09-1998 02-10-1996 30-06-1997 22-06-1995
WO 9741168 A	06-11-1997	AU 2928397 A CA 2252679 A CN 1217004 A EP 0900249 A	19-11-1997 06-11-1997 19-05-1999 10-03-1999
US 4720334 A	19-01-1988	NONE	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ BLACK BORDERS

☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

☐ FADED TEXT OR DRAWING

☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING

☐ SKEWED/SLANTED IMAGES

☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS

☐ GRAY SCALE DOCUMENTS

☐ LINES OR MARKS ON ORIGINAL DOCUMENT

☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.